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(54) Title: PROCESS FOR PREPARING LINEAR ALPHA-OLEFINS FROM ETHYLENE

(57) Abstract

Linear alpha-olefins are made by oligomerising ethylene using as catalyst a zirconium halide adduct and aluminium or zinc alkyl in the presence of a small amount of oxygen. The presence of the oxygen increases the linearity of the oligomers obtained.

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PROCESS FOR PREPARING LINEAR ALPHA-OLEFINS FROM ETHYLENE

This invention relates to the oligomerisation of ethylene to produce linear alpha-olefins.

It is known to oligomerize ethylene to produce linear alpha-olefins using a zirconium-containing catalyst, see, for example United States Patents Nos. 4486615, 4442309, 4434313, 4434312, 4410750, 4409409, 4396788, 4377720 and 4361714.

Japanese Patent Application No. 60-137683 (Idemitsu Petrochemical KK - Kokai 62-000430) discloses the production of linear alpha-olefins by polymerising ethylene in the presence of a mixture consisting of a zirconium halide, an alkyl aluminium halide and a compound of sulphur or nitrogen.

The present invention provides a process for the oligomerisation of ethylene to produce linear alpha-olefins having a very high degree of linearity. A high degree of linearity is important because ethylene oligomers are used as raw materials for preparing surfactants, e.g. ethoxylated linear alcohols, and linearity is necessary for the surfactants to be biodegradable.

In our European Patent Application No. 88305581.6 (Publication No. 295960) we have described and claimed a process for preparing substantially linear alpha-olefins having a number average molecular weight from about 70 to 700 by oligomerizing ethylene in the presence of a homogeneous two-component catalyst, the first component being an adduct of $ZrCl_aBr_b$, wh re a + b = 4 and a or b may be 0, 1, 2, 3 r

4, with an organic compound s lect d from the gr up consisting of esters, ket nes, ethers, amin s, nitriles, anhydrides, acid chlorides, amides or aldehydes, said organic compound having up to 30 carbon atoms and the second component being an alkyl metal catalyst selected from the group consisting of R_2AlX, $RAlX_2$, $R_3Al_2X_3$, R_3Al, and R_2Zn wherein R is C1-C20 alkyl and X is Cl or Br, the oligomerisation being conducted in a reactor vessel at 50 to 300° C at a pressure of about 500 to 5,000 psig in a solution of a C2-C100 alphaolefin or a liquid inert solvent which is not reactive with said catalyst and in which said two-component catalyst is soluble, the water content in the reactor vessel being such that the ratio of moles of zirconium to moles of water is at least 20 to 1. This process gives a mixture of ethylene oligomers having a high degree of linearity. It is, however, desirable still further to increase the linearity of the oligomeric product, especially in the case of the oligomers containing 12 to 18 carbon atoms.

It has now been discovered that the addition of a small amount of oxygen to the ethylene feed usefully increases the linearity of the oligomeric alpha-olefin product. The amount of oxygen present in ethylene ordinarily subjected to oligomerisation is no more than three parts per million by volume. The improved linearity characteristic of the present invention is obtained by using from about 10 to about 50 ppm

of xygen by volume based n the ethylene feed. While the addition f the xygen somewhat reduces the catalyst activity, this slight disadvantage is more than compensated by the improved linearity of the product.

The present invention accordingly provides a process for polymerizing ethylene to form a mixture of substantially linear alpha-olefin oligomers having a degree of polymerization from about to 3 to 30 which comprises contacting ethylene at a temperature of 50 to 250° and at a pressure of 3450 to 34500 kPa (500 to 5,000 psig) with a solution in an inert organic solvent of a two component catalyst in which the first component is an adduct of $ZrCl_aBr_b$, wherein each of a and b is 0, 1, 2, 3 or 4 and a + b = 4 with an organic compound of up to 30 carbon atoms selected from the group consisting of esters, ketones, ethers, amines, nitriles, anhydrides, acid chlorides, amides and aldehydes, and a second alkyl metal component selected from the group consisting of R_2AlX, $RAlX_2$, $R_3Al_2X_3$, R_3Al, and R_2Zn wherein R is alkyl or 1 to 20 carbon atoms and X is Cl or Br, the oligomerisation being conducted in the presence of 10 to 50 ppm by volume of oxygen based on the ethylene.

The first component of the catalyst used in the present invention is an adduct of $ZrCl_aBr_b$ with an ester, ketone, ether, amine, nitrile, anhydride, acid chloride, amide or aldehyde, and these various adduct-forming organic compounds

may have up to 30 carbon atoms. The adduct generally includes mole ratios of organic component to zirconium of from about 0.9 to 1 up to about 2 to 1. Equimolar adducts are preferred. The adduct must be soluble and stable in the solvent used as the reaction medium for the oligomerisation process of the invention. Suitable zirconium halides include $ZrCl_4$, $ZrBr_4$ and mixed halides such as $ZrClBr_3$, $ZrCl_2Br_2$ and $ZrCl_3Br$. Adducts of $ZrCl_4$ are especially preferred.

The organic compound used to form the adduct is preferably an ester of the general formula R_1COOR_2 wherein R_1 and R_2 are each alkyl, aryl, alkaryl, aralkyl of 1 to 30 carbon atoms and R_1 may also be hydrogen. R_1 and R_2 taken together may also represent a cycloaliphatic group and the ester may be a lactone such as gammabutyrolactone or phthalide. Especially preferred are alkyl acetate esters wherein the alkyl group has 6 to 16 carbon atoms, e.g. n-hexyl acetate, n-heptyl acetate, n-octyl acetate, n-nonyl acetate, n-decyl acetate, isohexyl acetate, isodecyl acetate and the like, which have been found to form dimeric equimolar adducts with $ZrCl_4$. Particularly preferred adducts may be represented by the formula $(ZrCl_4 \cdot CH_3COOR_1)_2$ where R_1 is C_6 to C_{16} alkyl or a mixture thereof. These preferred ester adducts are capable of providing highly concentrated solutions in the solvent used as the reaction medium, e.g. up to about 40 per cent by weight of $ZrCl_4$ wh n the preferred mixed isodecyl acetate esters are used. Particularly useful are mixtures of various

isomers of is hexyl, isoheptyl, isooctyl, isononyl, isodecyl or is tridecyl ac tate sold by Exxon Chemical Company, respectively, as Exxate[R] 600, Exxate[R] 700, Exxate[R] 800, Exxate[R] 900, Exxate[R] 1000 and Exxate[R] 1300. The isohexyl acetate mixture comprises about, by weight, 36 to 38 per cent n-hexyl acetate, 18 to 20 per cent 2-methyl-1-pentyl acetate. 22 to 24 per cent 3-methyl-1-pentyl acetate and 16 to 18 per cent 4-methyl-1-pentyl acetate as principal compounds. Exxate[R] 1000 isodecyl acetate mixture is a complex mixture of isomers and gas chromatographic analysis shows about a hundred different isomers being present, none of which are greater than about 10 per cent by weight of the mixture. Exxate 1000 has a boiling point range of about 218°C to 250°C (425°F to 482°F) (95 per cent distilled).

The adducts may be prepared by simple addition of the organic ester to a mixture of $ZrCl_4$ and the inert organic or alpha-olefin solvent. The ester is added slowly to the stirred mixture at room temperature and complete formation and dissolution of the adduct is observed within a few minutes. The dissolution is exothermic and the mixture can reach a temperature of about 50°C during the adduct formation.

Also suitable for providing soluble zirconium adducts useful as the first component in the catalysts used in the present invention are ketones, ethers and aldehydes which may be represented respectively by the formulae R_1COR_2, R_1OR_2 and

R_1COH wherein R_1 and R_2 each represent alkyl, aryl, alkaryl or aralkyl and a total number of carbon atoms in R_1 and R_2 is not more than about 30. Also suitable are primary, secondary and tertiary amines wherein the hydrocarbyl radicals have up to about 30 carbon atoms such as n-dodecyl amine and tri-n-hexyl amine. Also suitable are hydrocarbyl cycloaliphatic ethers and ketones having from 4 to 16 carbon atoms, e.g. cyclohexanone.

Other adduct forming organic compounds useful in the present invention include nitriles and hydrides, acid chlorides and amides having up to 30 carbon atoms. These may be represented by the formulae RCN, $(RCO)_2O$, RCOCl, $RCONH_2$, RCONHR and $RCONR_2$ where R represents a hydrocarbyl, alkyl, aryl, alkaryl or aralkyl group of up to 30 carbon atoms. Examples are n-undecane nitrile, n-decyl succinic anhydride and n-decanoyl chloride.

The second catalyst component used in the present invention is an aluminium alkyl of the formula R_2AlX, $RAlX_2$, $R_3Al_3X_3$, R_3Al or a zinc alkyl of the formula R_2Zn where R_1, R_2 and R_3 each represent alkyl of 1 to 20 carbon atoms and X is Cl or Br. Diethylaluminium chloride, aluminium ethyl dichloride and mixtures thereof are preferred.

The process of the present invention may be conducted under generally known oligomerisation conditions of temperatur and pressure, that is at a temperatur from about 50° to 250° C and under a pressure of 3450 to 34500 kPa (500 to 5,000 psig),

preferably 6900 to 24100 kPa (1,000 to 3,500 psig).

The pr cess is conducted in solution in an inert solvent which must be non-reactive with the catalyst system, and optionally in the presence of a solvent comprising a liquid alpha-olefin, especially a C_6-C_{100} alpha-olefin. Suitable solvents include aromatic or aliphatic hydrocarbons and halogenated aromatic hydrocarbons such as chlorobenzene, dichlorobenzene and chloro-toluene. Preferred solvents are toluene, xylenes and alkanes of 3 to 24 carbon atoms, especially heptane. Mixtures of these solvents may also be used.

Liquid alpha-olefins may also be used as solvents for the process, and these may include, more particularly, liquid alpha- olefins which have been formed by the oligomerisation process, especially those containing 6 to 30 carbon atoms. Such alpha- olefins may be used in admixture with the aforesaid non-reactive aromatic or aliphatic solvents. A useful solvent mixture comprises a minor proportion of C_4 to C_{30} alpha-olefins, such as about 10 per cent by weight of C_8 and C_{10} alpha-olefins and 0 to 5 per cent by weight of C_4 alpha-olefins, based on the amount of the ethylene feed stock, with a balance of the solvent being xylene. The use of this solvent mixture with solvent recycle improves distillation efficiency during product recovery.

The ethylene used in the present invention preferably contains not more than the following limits of impurities:

acetylenic hydrocarbons less than 1 part per million by weight; dienes less than 1 part per million by weight; carbon monoxide less than 5 parts per million by weight; carbon dioxide less than 15 parts per million by weight; oxygen-containing compounds (e.g. methanol, ethanol, acetone or sec-butanol) less than 1 part per million by weight; water less than 5 parts per million by weight; hydrogen less than 1 part per million by weight; oxygen less than 3 parts per million by weight; sulphur less than 5 milligrams per cubic meter; chlorine less than 5 milligrams per cubic meter. The water content of the ethylene is preferably reduced still further to less than 20 parts per billion before it is subjected to the oligomerisation, e.g. by contacting with 3A molecular sieve.

As already stated, in accordance with the present invention, the linearity of the alpha-olefin oligomers is improved by introducing into the reaction mixture from 10 to 50 parts per million by volume, preferably 20 to 40 parts per million by volume, of oxygen. The amount of catalyst used needs to be somewhat increased in order to compensate for the reduction of catalyst activity caused by the oxygen. For example, at about 40 ppm of oxygen by volume the catalyst concentration needs to be doubled to achieve the same degree of conversion as that obtained in the absence of the oxygen. At about 20 ppm of oxygen by volume, the proportion of catalyst should be increased by about 30 per cent.

The thylene and oxygen feed and th catalyst components may be introduced into the reaction vessel in any order, but preferably the ethylene, which may be pre-dissolved in the solvent, and the oxygen and the solution of zirconium tetrahalide adduct are first mixed and the second component of the catalyst, also in solution, is then added.

The temperature and pressure of the oligomerisation may be varied to adjust the molecular weight and yield of the desired product. The molecular weight (Mn) may also be controlled by adjustment of the molar ratio of the second component of the catalyst to the first component (i.e. of the aluminium or zinc to the zirconium).

The preferred reaction temperature for the production of high quality linear alpha-olefin oligomers having from 6 to 20 carbon atoms is about 120° to 250°C. At these preferred temperatures, the reaction pressure should be about 6900 kPa (1,000 psig) in a continuous stirred tank reactor. This produces about 20 per cent conversion of ethylene and limits the production of high molecular weight polyethylene to less than about 0.1 weight per cent of the product. In a tubular reactor, conversions of 65 to 80 per cent of ethylene at about 120° to 250°C can be achieved at pressures of about 20700 kPa (3,000 psig), depending upon the exact configuration of the reactor.

The amount of catalyst used is conveniently expressed as th w ight ratio of the ethyl ne feed to the zirconium in the

catalyst. Generally, from about 10,000 to 120,000 parts by weight f thylene are used per part by weight of zirconium in the catalyst, the preferred amount being from 25,000 to 35,000 parts by weight of ethylene per part by weight of zirconium and most preferably about 31,000 parts by weight of ethylene.

As already noted, the amount of water present in the reaction system should be reduced as far as possible since the catalyst is particularly sensitive to water. Small amounts of water tend to increase the production of the undesired high molecular weight polyethylene and reduce conversion to the desired linear alpha-olefins.

The relative amounts of the two catalyst components used in the process of the invention can be varied, but a mol ratio of the second component to the first component from about 1 : 1 up to about 50 : 1 is generally used, the preferred ratio being from about 10 : 1 to about 25 : 1.

During the reaction the mol ratio of the ethylene feed to the oligomerisation product should be maintained at about 0.8 in order to minimize copolymerisation reactions which might interfere with the achievement of the desired high degree of linearity of the product. Preferably this ratio is greater than 2.

The linear alpha-olefin oligomerisation product may be isolated by conventional procedures, e.g. use of an aqueous caustic catalyst quench followed by water washing and

recovery of the final product by distillati n.

The invention is illustrated by the following Examples:

EXAMPLES

A series of ethylene oligomerizations were conducted in a 1-liter stirred autoclave at the temperatures and pressures indicated in the Table below. Reactor volume was controlled at about 500 cc by a dip leg which served as the reactor exit. The autoclave was electrically heated and oil cooled. Pressure and temperature were automatically controlled. Polymer grade ethylene was compressed to about 200 barg from a bank of 60 barg cylinders. After compression, the ethylene gas was passed over a bed of molecular sieves to remove water to less than 1 ppmv. The moisture content was monitored continuously using aluminium oxide sensors. The oxygen content of the ethylene was also continuously monitored using a on-line oxygen meter and was less than 3ppmv. Ethylene was fed continuously at a measured rate to the reactor during the test runs. Reaction solvent was dried over molecular sieves to less than 1 ppmw and then metered continuously into the reactor. Catalyst and co-catalyst solutions were prepared in a dry box using heated and evacuated glassware to ensure minimum water contamination. The zirconium catalyst was diluted in dry solvent (solvent dried to less than 1 ppmw over molecular sieves) to a concentration of about 20 x 10^{-6} gram moles of zirconium per gram of solution. The solutions were th n transferr d to the reactor fe d tanks and held

und r a nitrog n blanket. Th Zr catalyst s luti n was f d to the reactor at 10 to 100 cc/hr. The aluminium co-catalyst solutions were prepared from concentrated stock solutions obtained from a commercial supplier. Again, dilution solvent was dried to less than 1 ppmw water content before use. Co-catalyst was generally diluted to about 200 x 10^{-6} gram moles of aluminium per gram of solution. The diluted solution was transferred to the reactor at 10 to 100 cc/hr. A test run was started by feeding solvent, ethylene, and co-catalyst to the reactor during a heat-up period lasting up to several hours. Then, the Zr catalyst feed was started. A run balance period for data collection was started after steady state was achieved, generally 1-2 hours after the oligomerization was initiated, as noted by the reaction temperature. The catalyst used was a equimolar complex of Zirconium tetrachloride and isodecyl acetate isomers (Exxate[R] 1000 of Exxon Chemical Company) and aluminum diethyl chloride. The ethylene solvent ratio was 1:1 by weight. The following Table shows for for 25 runs carried out in the absence of added oxygen: the reaction temperature, the reaction pressure in bars gauge, the aluminum: zirconium molar ratio, the weight percent conversion of ethylene into

oligom rs, the catalyst activity in t rms f kilograms f oligomer product per gram of Zirconium in the catalyst per hour, and the number average molecular weight of the oligomeric product.

TABLE 1

RUN NO	T °C	P barg	Al/Zr molar	Conv. wt %	Catalyst Activity Kg/g Zr/h	$\bar{M}n$ of product
1	172	187	13.8	77	225	102
2	171	188	14.8	52	168	102
3	171	188	14.8	68	184	103
4	171	188	14.3	40	158	100
5	171	187	12.7	73	177	105
6	171	186	13.9	82	152	114
7	172	187	16.3	84	182	110
8	171	185	18.8	55	183	100
9	171	186	17.8	74	193	102
10	171	189	16.0	77	189	104
11	171	189	13.6	69	182	105
12	171	188	13.6	82	187	107
13	170	188	12.3	85	171	113
14	170	185	14.0	62	160	109
15	171	190	14.9	74	199	107
16	170	187	12.2	83	179	112
17	175	188	14.6	80	168	110
18	171	188	13.0	85	177	116
19	171	189	13.7	82	164	113
20	171	186.5	11.6	73.5	169	110
21	171	188	12.2	66.5	141	107
22	171	190	12.3	87	165	112
23	171	188	10.8	80.5	151	110
24	171	188.5	11.5	72.5	159	110
25	171	188.5	11.1	70.0	147	112

For each run the proportic.is of linear alpha-olefins, linear internal olefins, and branched olefins wer determined. Th proportions of branched olefins obtained in each run are shown in the following Table:

TABLE 2

FRACTION OF BRANCHED ISOMERS, WT%
based on total oligomers of the
indicated carbon number

RUN NO	C6	C8	C10	C12	C14	C16	C18
1	1.6	2.7	6.4	9.4	13.9	18.2	22
2	0.9	1.5	3.6	5.4	8.4	11.2	13.6
3	1.4	2.5	5.6	8.3	12.4	16.5	20.6
4	0.7	1	2.7	4.2	6.5	8.8	11.7
5	1.2	1.6	4.9	7.3	11.2	14.6	18.5
6	2.8	4.8	9.8	14.2	21	26.6	31.7
7	2.5	4.4	9.2	13.3	19.6	25	30.2
8	1.3	2	4.5	6.8	10.2	13.5	17.3
9	1.7	2.7	6.6	9.8	14.3	19	23.4
10	1.7	2.4	6.9	10.3	15.2	19.8	24.2
11	1.4	2.1	5.7	8.5	12.8	16.9	20.8
12	1.8	2.6	7.2	10.6	15.8	20.6	25.3
13	2.5	4	9.5	13.8	20.2	25.9	31.2
14	1	1.5	3.7	5.6	8.6	11.4	15.3
15	1.6	2.4	5.4	8	11.6	15.7	19.5
16	2.2	2.9	8.4	12.2	17.6	23.3	28.5
17	2.1	3.7	8.2	11.9	17.6	22.8	27.9
18	2.3	3.7	8.8	12.7	18.9	24.3	29.2
19	2.1	3.4	8	11.7	17.3	22.4	27.3
20	1.4	1.9	5.7	8.5	12.8	16.8	20.7
21	1.3	1.4	4.9	7.4	11.1	14.7	18.5
22	2.2	3.8	8.6	12.4	18.3	23.7	28.6
23	1.5	1.7	5.8	8.5	13	17.1	20.1
24	1.4	2.2	5.4	8	11.8	15.9	19.2
25	1.3	1.4	4.9	7.3	11.1	14.7	18.3

In the further seri s of experiments oxyg n was add d to the reaction mixture in a proportion of 37, 21 or 23.5 parts per million by volume based on the ethylene. The reaction conditions were otherwise identical except that the Zr and Al catalyst concentration had to be doubled in the case of 37 ppm by volume of oxygen and had to be increased by 30% in the case of 21 or 23.5 ppm by volume of oxygen at achieve comparable conversion levels. This oxygen was deliberately added to ethylene feed and continuously monitored during the runs. The following Table shows, for each run, the proportion of added oxygen, the reaction temperature, the pressure in bars gauge, the mol ratio of aluminium to zirconium in the catalyst, the weight percentage conversion of the ethylene feed, the activity of the catalyst in kilograms of oligomeric product per gram of zirconium per hour, and the number average molecular weight of the oligomers obtained:

TABLE 3

RUN No	O_2 ppmw	T °C	P barg	Al/Zr molar	$C_2^=$ Zr wt. ratio	Conversion wt %	Catalyst Activity Kg/g Zr/h	Mn
26	37	170	184	13.7	64,641	1.3	3.6	116
27	37	171	186	13.4	32,362	79	69	131
28	37	171	190.5	13.0	33,300	64	62	126
29	37	171	189	13.0	33,300	82	70	140
30	21	171	189.5	13.7	43,956	78	89	115
31	21	171	190	13.7	43,956	85	90	119
32	21	171	190	13.7	43,956	86.5	98	123
33	23.5	173	190	14.3	49,950	70	94	117

The data for Run no. 26 are includ d for comparison. They show that, in the presence of 37 ppmw of oxygen, if too small an amount of the catalyst is used, the percentage conversion becomes very small.

The following Table shows the proportions of branched isomers obtained for each of runs 27 to 33:

TABLE 4

FRACTION OF BRANCHED ISOMERS, WT% based on total obligomers of the indicated carbon number

RUN NO	C6	C8	C10	C12	C14	C16	C18
27	1	1.2	3.8	5.6	8.9	11.8	14.5
28	0.9	0.9	2.5	3.8	6.1	7.8	10.1
29	1	1.1	3.7	5.6	9	11.1	14.5
30	0.9	1.2	4.8	4.9	7.6	10.1	12.8
31	1.3	1.7	5.2	7.8	12	15.7	19.3
32	1.5	2	6.2	9.1	13.9	18.2	22.4
33	1	1.1	3.7	5.6	8.6	11.2	14.3

In general, the proportion of linear olefins obtained decr ases and that of branched olefins obtained incr ases as the conversion rate of the ethyl n increases. The am unt of internal linear olefins which can be calculated by subtracting the total amount of alpha and branched isomers of a given carbon number from 100, remains the same with or without oxygen being present. For any particular conversion rate, the addition of oxygen to the reaction mixture in accordance with the present invention increases the alpha linearity of the oligomers obtained. This is illustrated in the accompanying rawings, Figures 1 and 2 show the weight percentage of linear alpha-olefins plotted against weight percentage conversion of the ethylene feed and: Figures 3 and 4 show the weight percentage of branched olefins plotted against the weight percentage conversion of the ethylene feed. In each Figure the solid lines represent the weight percentage of linear (Figures 1 and 2) or branched (Figures 3 and 4) olefins to be expected in the absence of oxygen. The plotted points show the results obtained in the presence of oxygen as given above in Tables 3 and 4. Figures 1 and 3 relates to oligomers having 8, 12 or 18 carbon atoms and Figures 2 and 4 relates to oligomers having 6,10, 14 and 16 carbon atoms. In each case the increased linearity or reduction in branching achieved by the presence of the oxygen is clearly shown.

CLAIMS

1. Process for a polymerizing ethylene to form a mixture of substantially linear alpha-olefin oligomers having a degree of polymerization from about 3 to 30 which comprises contacting ethylene at a temperature of 50 to 250°C and at a pressure of 3450 to 34500 kPa (500 to 5,000 psig) with a solution in an inert organic solvent of a two component catalyst in which the first component is an adduct of $ZrCl_aBr_b$, wherein each of a and b is 0, 1, 2, 3 or 4 and a + b = 4 with an organic compound of up to 30 carbon atoms selected from the group consisting of esters, ketones, ethers, amines, nitriles, anhydrides, acid chlorides, amides and aldehydes, and the second component is an alkyl metal component selected from the group consisting of R_2AlX, $RAlX_2$, $R_3Al_2X_3$, R_3Al, and R_2Zn wherein R is alkyl or 1 to 20 carbon atoms and X is Cl or Br, the oligomerisation being conducted in the presence of 10 to 50 ppm of oxygen by volume based on the ethylene.

2. Process according to claim 1 in which the proportion of oxygen is 20 to 40 ppm by volume based on the ethylene.

3. Process according to claim 1 or 2 wherein the weight ratio of ethylene to zirconium is about 10,000 : 1 to 120,000 : 1.

4. Process according to claim 3 wherein the said ratio is from 25,000 : 1 to 35,000 : 1.

5. Process according to any one of the prec ding claims wherein, in the said first component, th said organic compound is an ester of the formula RICOOR2 wherein each of R1 and R2 is alkyl, aryl, alkaryl, aralkyl and R1 may also be hydrogen, the total number of carbon atoms in R1 and R2 being from 1 to 30.

6. Process according to any one of claims 1 to 4 wherein the said first component is an adduct of $ZrCl_4$ and an acetate ester of the formula CH_3COOR_1 wherein R1 is alkyl or 6 to 16 carbon atoms.

7. Process according to claim 6 wherein the said acetate ester is a mixture of isomers of isodecyl acetate.

8. Process according to any one of the preceding claims wherein the said inert solvent is toluene, xylene, or an alkane of 3 to 24 carbon atoms.

9. Process according to any one of the preceding claims wherein the second catalyst component is diethyl aluminium chloride or ethyl aluminium dichloride or a mixture thereof.

10. Process according to any one of the preceding claims wherein the oligomerization is effected at a temperature of 120 to 250°C and under a pressure of 6900 to 24100 kPa (1,000 to 3,500 psig).

FIG.1

LINEARITY VS CONVERSION

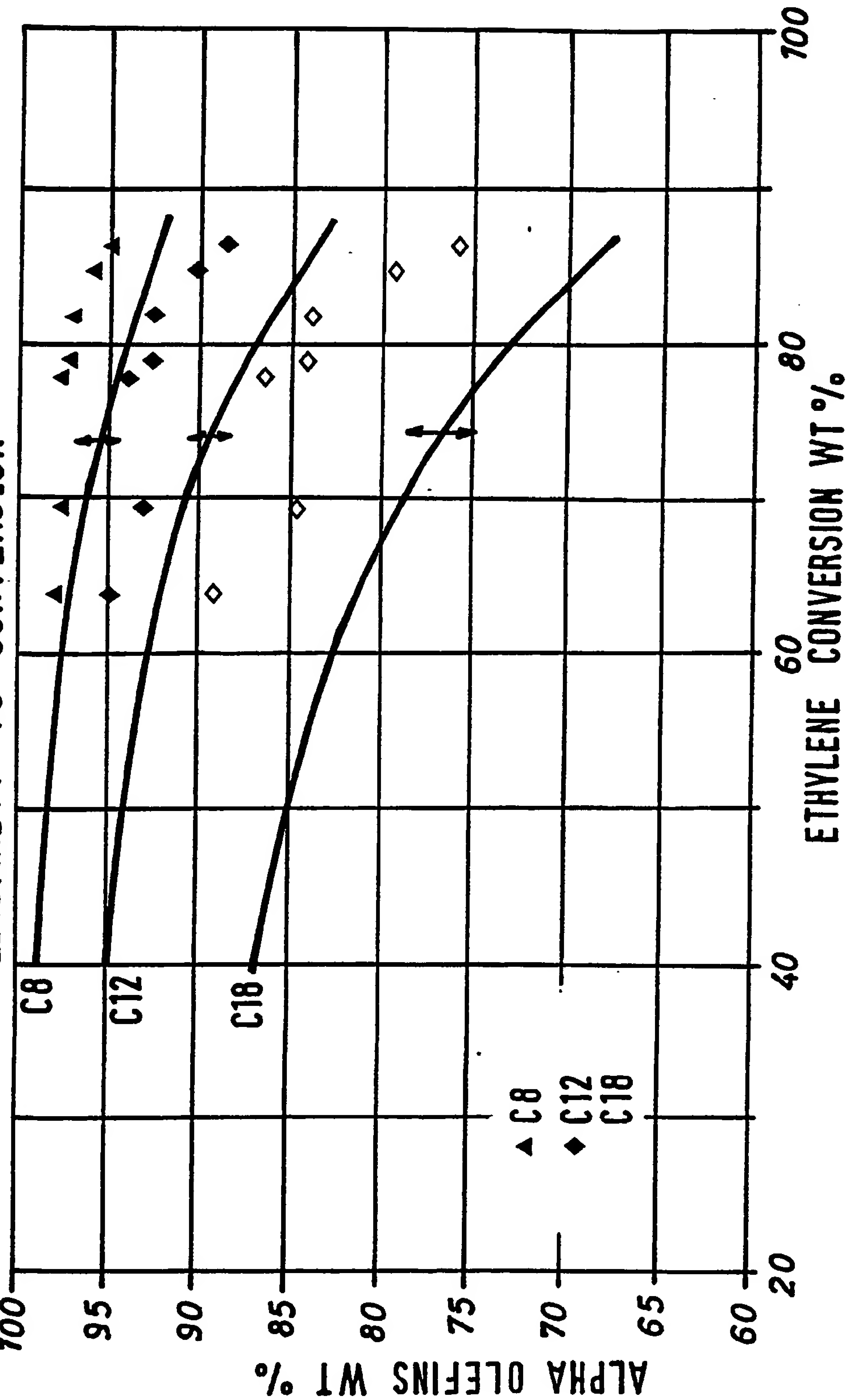


FIG.2

LINEARITY VS CONVERSION WITH O2 POISON

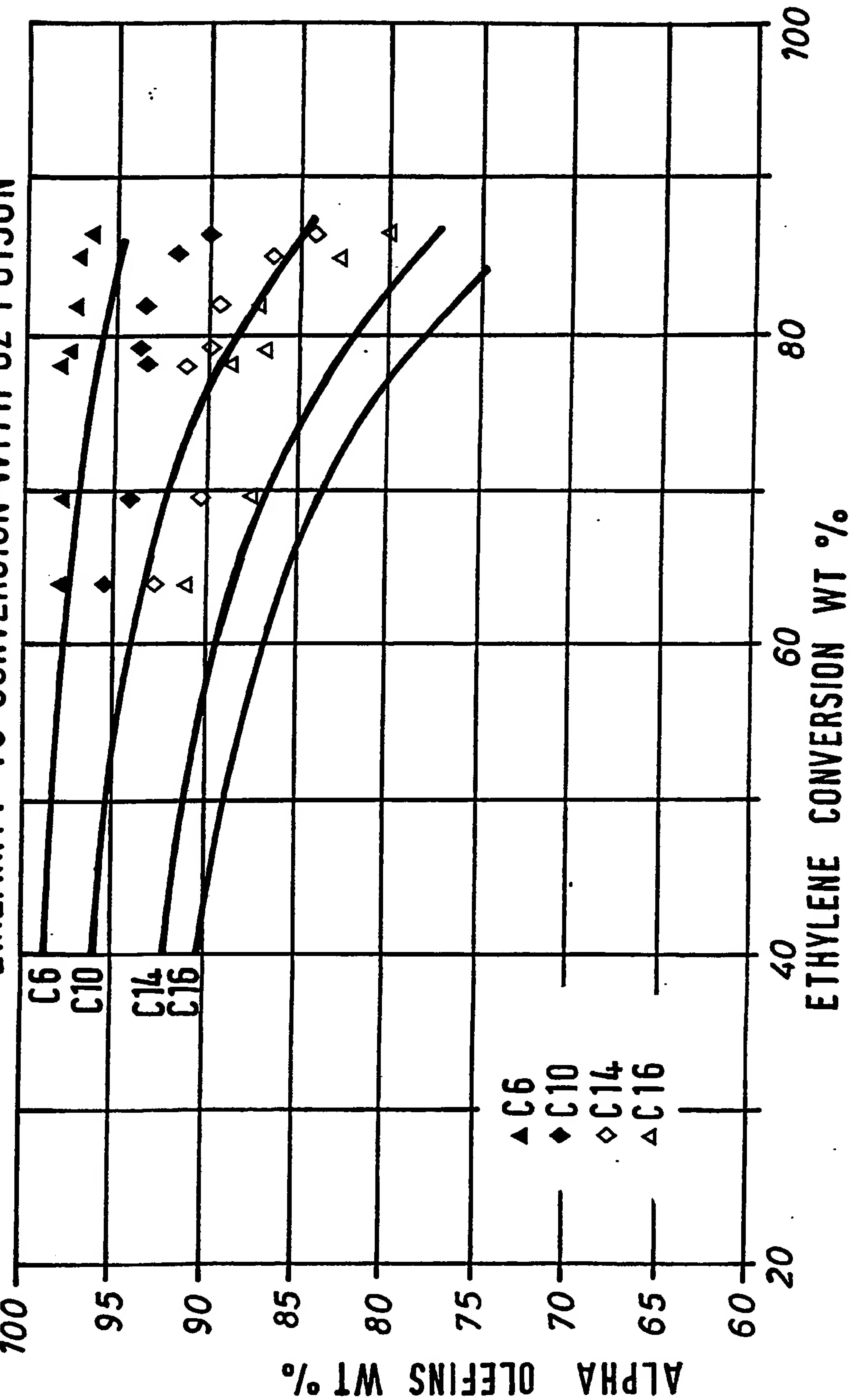


FIG.3
BRANCHINESS VS CONVERSION

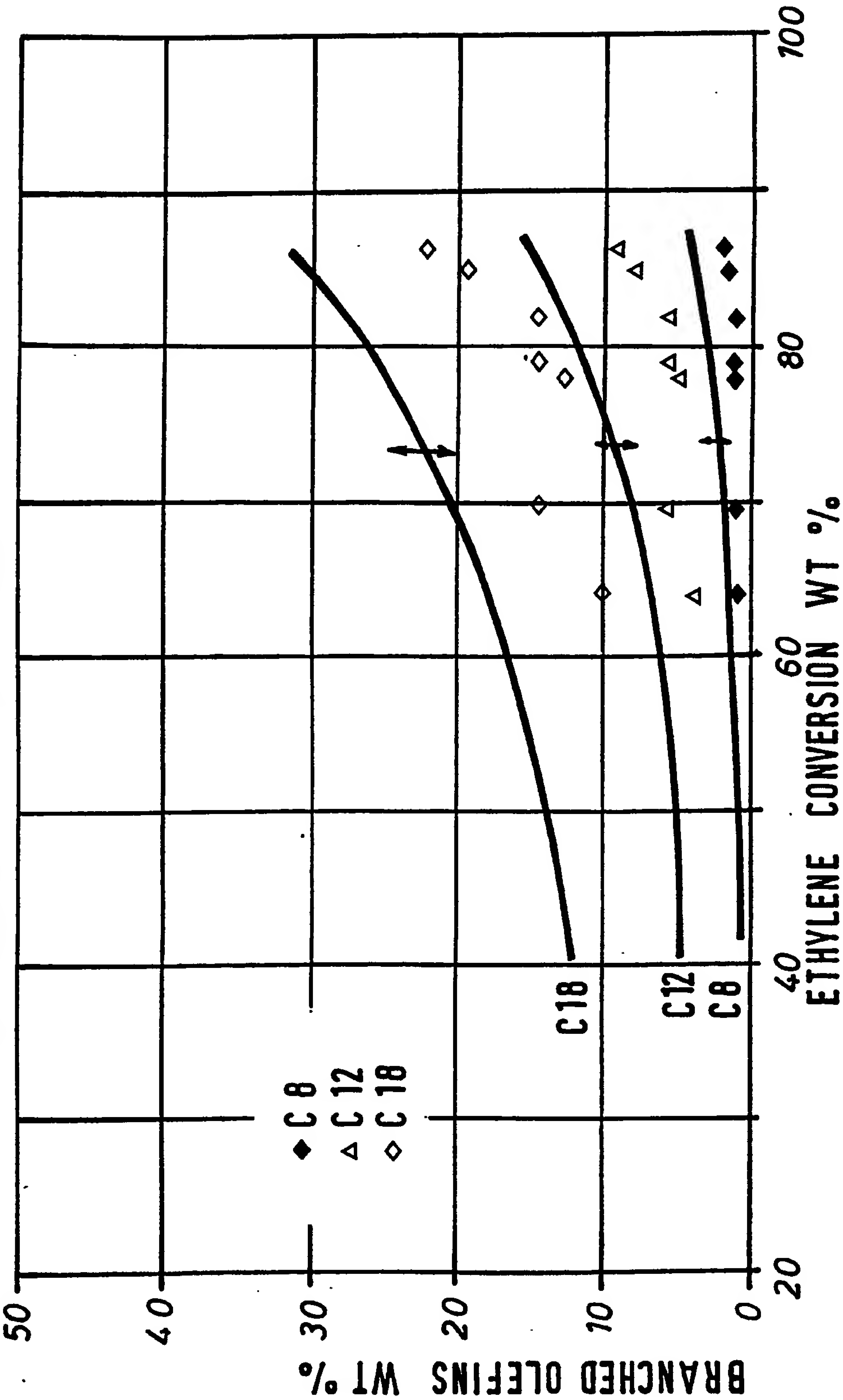
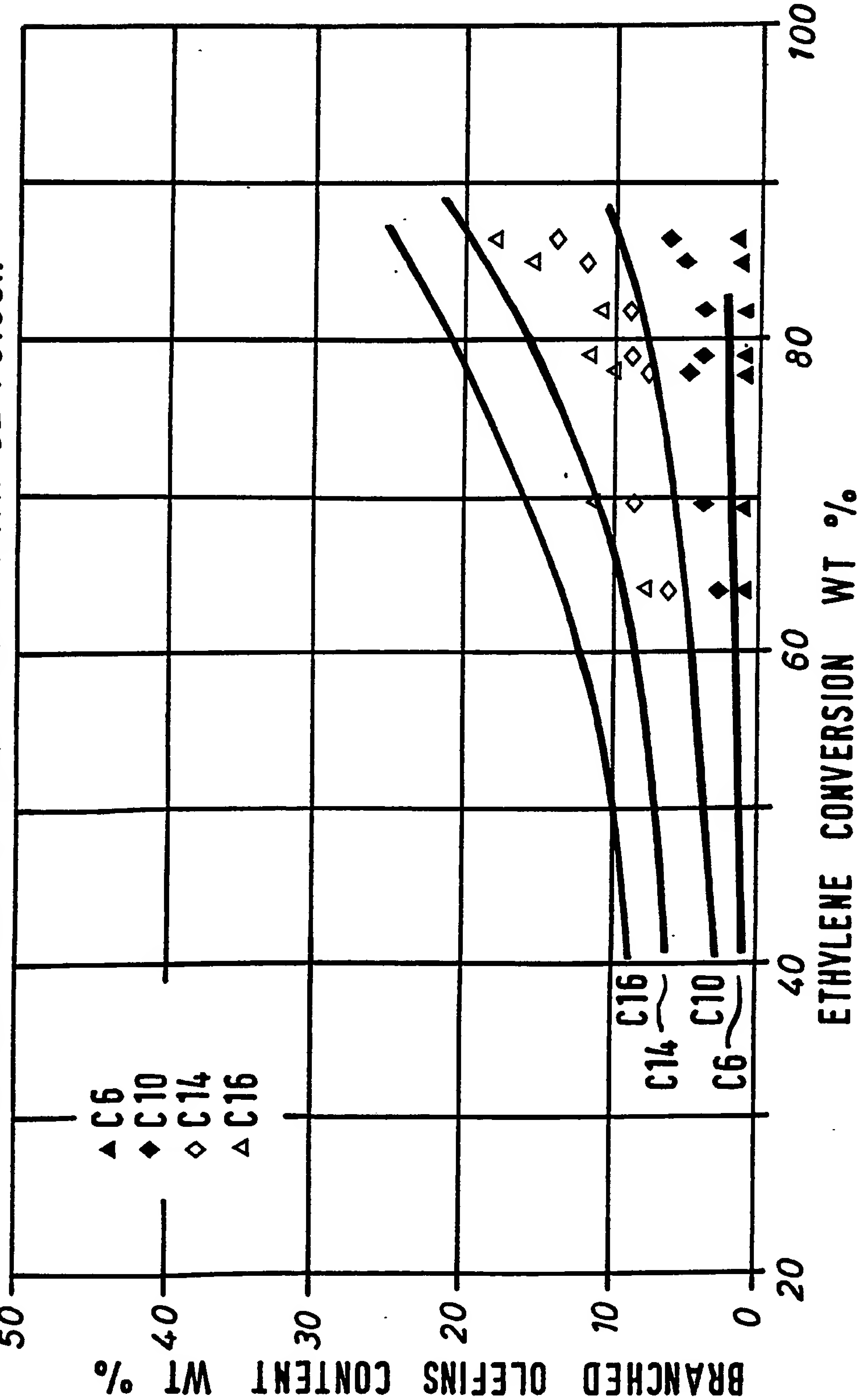


FIG.4

BRANCHINESS VS CONVERSION WITH O2 POISON



INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 90/01284

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^5: C 07 C 2/30

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^5	C 07 C 2/00

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [*]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	EP, A, 0295960 (EXXON CHEMICAL PATENTS INC.) 21 December 1988 see claims (cited in the application)	1,3-10

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* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
26th October 1990	23. 11. 90
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	M. TORIBIO

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. GB 9001284 SA 39128

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 13/11/90
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0295960	21-12-88	US-A- 4855525	08-08-89
		AU-B- 598676	28-06-90
		AU-A- 1697888	22-12-88
		JP-A- 1063532	09-03-89

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82